

## PHYSICO-MECHANICAL PROPERTIES OF BLENDED SLAG CEMENT AND PLAIN CEMENT IN 5% SODIUM SULPHATE SOLUTION

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### ABSTRACT

*The effect of aggressive media which contain 5 % NaSO<sub>4</sub> solution on ordinary Portland cement and slag cement was studied by the determination of bulk density, total porosity and compressive strength up to 90 days. The results in this paper pointing to the harmful effect in presence of sodium cations. This is mainly due to the reaction between the cement matrix CSH and Na<sup>+</sup> ion. Furthermore the aggressive medium gets negative effect on the hydration process in all types of cement. In addition, ordinary Portland cement highly effected compared to other types of cement. These results have been confirmed through the IR and SEM.*

**KEYWORDS:** Mechanical Properties; Slag Cement, Plain Cement, Sulphate Attack

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### INTRODUCTION

In the production of iron, iron ore, iron scrap, and fluxes (limestone and/or dolomite) are charged into a blast furnace along with coke for fuel [1]. The coke is combusted to produce carbon monoxide, which reduces the iron ore to a molten iron product. This molten iron product can be cast into iron products, but is most often used as a feedstock for steel production. The blast furnace slag is a secondary product resulting from the steel industry and produced in huge amounts every year. Therefore, the use of these wastes in any industry saves money and preserves the environment. It consists primarily of silicates, aluminosilicates, and calcium-alumina-silicates. The molten slag, which absorbs much of the sulfur from the charge, comprises about 20 percent by mass of iron production. Different forms of slag product are produced depending on the method used to cool the molten slag. These products include air-cooled blast furnace slag (ACBFS), expanded or foamed slag, pelletized slag and granulated blast furnace slag (GBFS).

Ground granulated blast furnace slag is a finely ground, rapidly chilled aluminosilicate melt material separated from molten iron in the blast furnace as a by-product. Rapid cooling results in an amorphous or a glassy phase known as GGBFS or water-cooled slag (WCS) [2].

The present work aims to study the physico-mechanical properties of different cement paste.

### EXPERIMENTAL PROCEDURE

#### Materials Used

Materials used in this investigation were ground granulated blast furnace slag (WCS) which produced

from Iron and Steel Company and Plain Cement (OPC) produced from National Cement Company. On the other side, air-cooled blast furnace slag (ACBFS) used as reference sample. The chemical analyses of these raw materials are shown in Table 1.

**Table 1: Chemical Composition of Starting Materials, (wt %)**

Chemical Composition (%)	Types of Cement		
	OPC	WCS(Slag A)	ACBFS(Slag B)
Na <sub>2</sub> O	0.601	1.399	0.566
MgO	2.208	5.501	1.156
Al <sub>2</sub> O <sub>3</sub>	4.227	12.137	3.749
SiO <sub>2</sub>	15.892	31.303	15.907
P <sub>2</sub> O <sub>5</sub>	0.175	0.020	0.355
SO <sub>3</sub>	2.539	2.358	2.614
K <sub>2</sub> O	0.103	1.356	0.197
CaO	67.330	33.179	66.986
TiO <sub>2</sub>	0.510	0.607	0.516
MnO	0.047	5.547	1.038
Fe <sub>2</sub> O <sub>3</sub>	5.292	0.504	6.467
BaO	0.019	5.730	0.169

### Preparation of Samples

Different mixtures were prepared from ground granulated slag (WCS) or reference granulated slag (ACBFS) with Ordinary Portland Cement (OPC).

### Preparation of Cement Pastes

A weight amount of cement was placed on a smooth, non absorbent surface, and a crater was formed in the center. The required amount of mixing water was poured into crater by aid of trowel. The paste cement was placed in the mould until homogeneous specimen was obtained after the top layer was compacted; the surface of the paste was made smooth and even with the top surface of the mould by the aid of thin edged trowel. Immediately after molding specimens were cured in a humidifier at room temperature for 24 hours. At the end of the moist curing period, the cubes were demoulded and curing was continued under water for the required time of testing. During the effect of aggressive medium, the cube 2.5 cm (1 inch-sides length) were demolded and curied under water about 28 days, then the cube was immersed in 5 % Sodium sulphate solution freshly prepared up to 90 days.

### Methods of Physico- Mechanical Properties

#### Bulk Density

Bulk density is defined as the mass (weight) of the dry solids divided by the total volume of the wet sample. The bulk density can be determined by dividing the mass of dry cement particles on the volume of cement sample[3].

$$\text{Bulk Density g/cm}^3 = M_d / V$$

Where;

M<sub>d</sub>= mass of dry cement sample (g).

V= total volume (volume of the wet sample) cm<sup>3</sup>.

### **Water Absorption and Total Porosity**

The water absorption was determined according to **Shebl et al.[4]**. The samples were immersed in a water bath for 24 h. The samples were then removed from the water allowing it to drain. A damped cloth was used to remove any visible surface water. The weight of the samples was recorded as saturated weight ( $W_s$ ). The samples were dried in a ventilated oven at 80°C for 1 day. The final weight of the samples was recorded as dry weight ( $W_d$ ). The water absorption is calculated from the following equation:

$$\text{Water absorption} = [(W_s - W_d) / W_d] \times 100$$

After the determination of water absorption of specimens, total porosity of the hardened cement pastes, could be measured by the equation:

$$\text{Total Porosity \%} = W_s - W_d / \rho_w V$$

Where;  $\rho_w$  is the water density; V the volume of the sample.

### **Compressive Strength Measurements**

The compressive strength measurements were carried out by preparing neat cement cubes 2.5× 2.5 × 2.5 cm, which were cured for 24 h, demoulded and continuously cured in a humidity chamber till the time of testing. A set of 3 cubes were used for each compressive strength determination[5]. Compressive strength measurements were carried out using two tones Amsler testing machine with a loading rate of 100 kg/min determined according to **Khater et al.[2]**.

### **Spectroscopic Analysis**

#### **Infrared Spectroscopic Analysis**

The infrared spectrum of compound can be used as a finger print to provide qualitative and quantitative analysis of mixture. IR spectral analysis was carried out for some selection sample of hydrated pastes to provide additional information on the hydrated products, and it is sometimes possible to have conclusions concerning aspects of the structure from their appropriate spectrum. The samples were prepared using alkali halide (KBr) pressed disk techniques as it gives a further reduction in scattering. 1.0 mg of the hydrated powder sample was ground with 99 mg of potassium bromide in an agate mortar to produce a homogeneous mixture. The mixture was pressed under vacuum to give a transparent disk of 1.0 cm in diameter. Transfer the KBr disc to a sample holder and place it in the spectrometer. The infrared spectral analysis was recorded from KBr discs using Genesis-II IR spectrometer in the range 400-4000  $\text{cm}^{-1}$ .

#### **Scanning Electron Microscope (SEM) Analysis**

The SEM was used to observe the surface morphology and the grain size. The examination was carried out on different samples using JEOL JSM 5410 (Japan). The data that presented and discussed in this paper are divided into two main parts. The first part is concerned with determining the mechanical properties for many designed mixtures containing both types of slag with OPC.

## **RESULTS AND DISCUSSIONS**

### **Physico-Mechanical Properties**

The influence of aggressive attack has been studied on blended slag cement pastes and OPC pastes immersed in 5% sodium sulphate solution up to 90 days. In the beginning, samples of hardened cement pastes were cured under tap

water up to 28 days (zero time), then immersed in 5 % sodiumsulphate solution as aggressive medium up to 3, 7, 15, 28, 60 and 9 days. The mix design of blended slag cement and plain cement are given in Table 2.

**Table 2: Mix Design of Blended Slag Cement and Plain Cement**

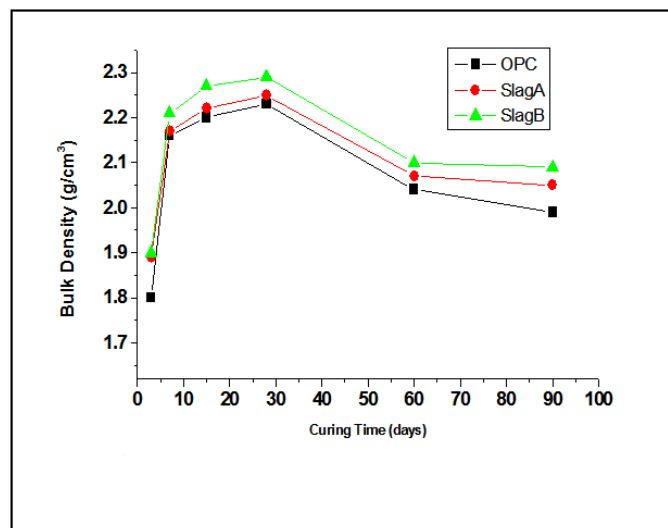
Slag A	(95% OPC+ 5% WCS)
Slag B	Reference sample (95% OPC+5% ACBFS)
OPC	100% OPC

### Bulk Density

The values of bulk density of the hardened blended slag cement and plain cement pastes cured in tap water up to 28 days (zero time), then immersed in 5% sodium sulphatesolution up to 90 days are shown in (3) and graphically plotted as a function of curing time in Figure 1.

**Table 3: Bulk Density ( $\text{g/cm}^3$ ) of Hardened Blended Slag Cement and Plain Cement Pastes Immersed in 5 % Sodium Sulphate as a Function of Curing Time**

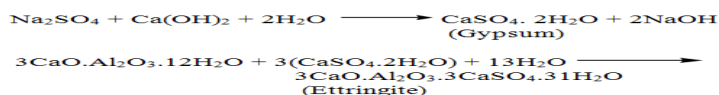
Immersing Time (days)	Bulk Density ( $\text{g/cm}^3$ )		
	OPC	Slag A	Slag B
3	1.80	1.89	1.90
7	2.16	2.17	2.21
15	2.20	2.22	2.27
28	2.23	2.25	2.29
60	2.04	2.07	2.10
90	1.99	2.05	2.09



**Figure 1: Bulk Density ( $\text{g/cm}^3$ ) of Hardened Blended Slag Cement and Plain Cement Pastes Immersed in 5% Sodium Sulphate as a Function of Curing Time**

The results indicate that, the bulk density of the plain cement increases up to 28 days then decreases gradually with time up to 90 days. The increase in bulk density is mainly due to increasing in the amount products which were formed and precipitated in the pores originally filled with water leading to an increase in the bulk density up to 28 days. After that, the hydration products react with the salt solution sodium sulphate to form gypsum and ettringite.

According to the following reaction [6]:



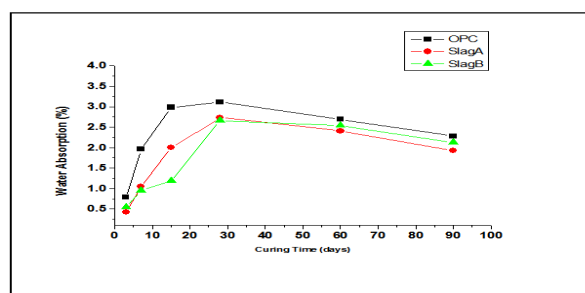
In blended slag cement the bulk density increases up to 28 days, then decreases with time up to 90 days. The increase in bulk density at early days may be attributed to the hydration of slag cement to form (CSH) which increases the bulk density. The amount of bulk density decreases in blended water slag cement due to the effect of aggressive attack of sodium sulphate solution. This is mainly due to the formation of gypsum and ettringite, which decreases the bulk density values. The comparison between blended slag cement and plain cement, the decreases in bulk density in plain cement are easily noted compared with blended slag cement, this is may be due to decrease in the amount of sulphaaluminate hydrates which produces from ordinary Portland cement in aggressive media.

### Water Absorption

The values of Water absorption of the hardened blended slag cement and plain cement pastes cured in tap water up to 28 days (zero time), then immersed in 5% sodium sulphatesolution up to 90 days are given in Table 4 and graphically plotted as a function of curing time in Figure 2.

**Table 4: Water Absorption (%) of Hardened Blended Slag Cement and Plain Cement Pastes Immersed in 5 % Sodium Sulphate as a Function of Curing Time**

Immersing Time (Days)	Water Absorption (%)		
	OPC	Slag A	Slag B
3	0.783	0.426	0.552
7	1.965	1.043	0.953
15	2.984	2.003	1.185
28	3.112	2.735	2.666
60	2.695	2.409	2.539
90	2.281	1.928	2.124



**Figure 2: Water Absorption (%) of Hardened Blended Slag Cement and Plain Cement Pastes Immersed in 5% Sodium Sulphate as a Function of Curing Time**

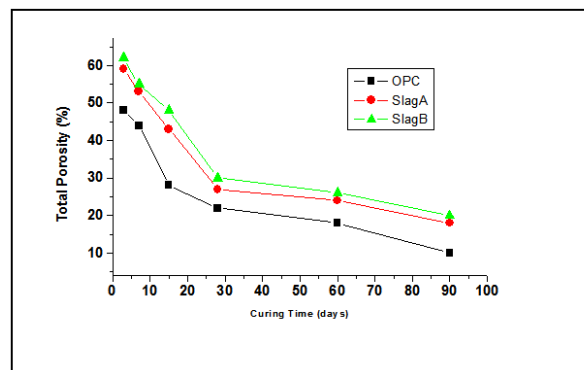
The water absorption values increase up to 28 days and then decrease up to 90 days for OPC and blended slag cement. This due to fine particles of pozzolan block the channels connecting capillary pores in cement paste and generate more homogenous distribution of CSH gel resulting in less pore structure and permeable voids [7].

### Total Porosity

The values of total porosity of the hardened blended slag cement and plain cement pastes cured in tap water up to 28 days (zero time), then immersed in 5% sodium sulphate up to 90 days are given in Table 5 and graphically plotted as a function of curing time in Figure 3.

**Table 5: Total Porosity (%) of Hardened Blended Slag Cement and Plain Cement Pastes Immersed in 5 % Sodium Sulphate as a Function of Curing Time**

Immersing Time (Days)	Total Porosity (%)		
	OPC	Slag A	Slag B
3	48	59	62
7	44	53	55
15	28	43	48
28	22	27	30
60	18	24	26
90	10	18	20

**Figure 3: Total Porosity (%) of Hardened Blended Slag Cement and Plain Cement Pastes Immersed in 5% Sodium Sulphate as a Function of Curing Time**

In plain cement (OPC) case pastes immersed in 5% sodium sulphate solution, the total Porosity decreases with curing time. The decreases in porosity are mainly due to the precipitation of hydrated phases into the variable pores of cement pastes. The decrease in porosity during the later age is very slight due the formation of ettringite and soluble compound. The formation of ettringite increases the volume that causes the cracking in cement.

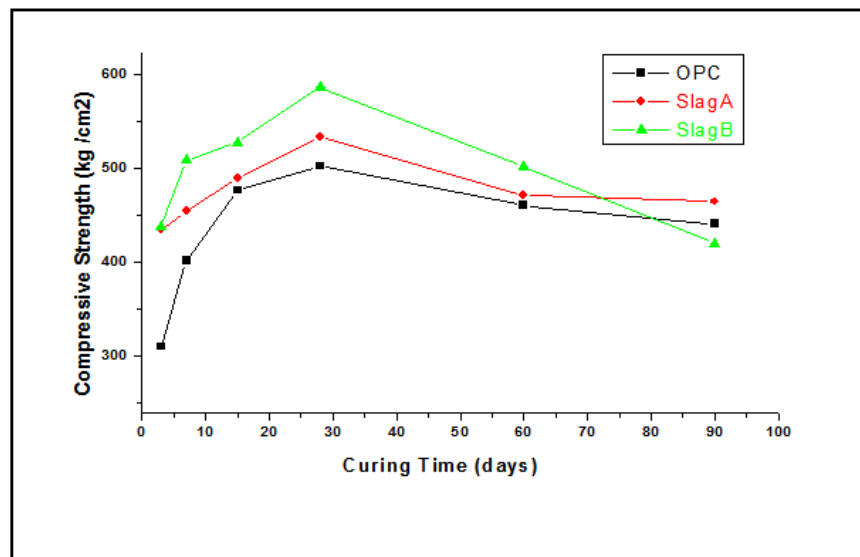
In case of blended slag cement, the total Porosity decreases up to 90 days. The decrease in total porosity at early age is sharply due to the hydration of slag, which reacts with Portlandite to form CSH.

### Compressive Strength

The values of compressive strength of the hardened blended slag cement and plain cement pastes cured in tap water up to 28 days (zero time), then immersed in 5% sodium sulphate up to 90 days are given in Table 6 and graphically plotted as a function of curing time in Figure 4.

**Table 6: Compressive Strength (kg /cm<sup>2</sup>) of Hardened Blended Slag Cement and Plain Cement Pastes Immersed in 5 % Sodium Sulphate as a Function of Curing Time**

Immersing Time (Days)	Compressive Strength (kg /cm <sup>2</sup> )		
	OPC	Slag A	Slag B
3	310	435	438
7	402	455	509
15	477	490	528
28	503	534	587
60	461	472	502
90	441	465	420



**Figure 4: Compressive Strength (kg/cm<sup>2</sup>) of Hardened Blended Slag Cement and Plain Cement Pastes Immersed in 5% Sodium Sulphate as a Function of Curing Time**

The results can be summarized as following:

The gain in the strength for the samples having OPC mainly attributed to the hydration of aluminate, ferroaluminate and C<sub>3</sub>A in addition to calcium silicate phase. The hydration product fills the pores and at the same time having binder characteristic.

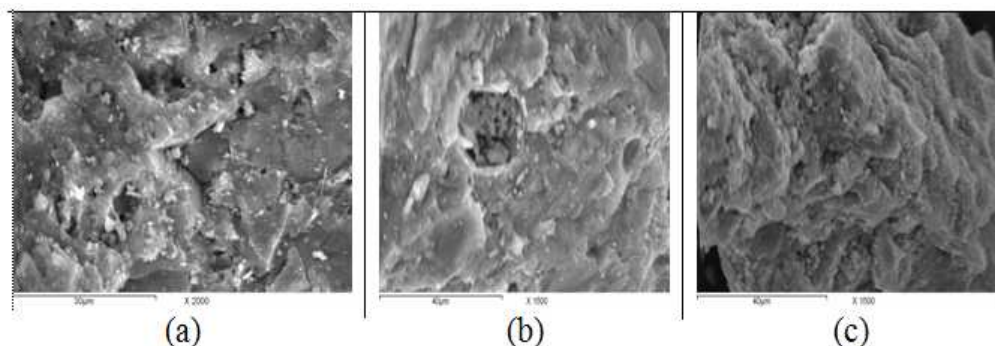
The compressive strength of OPC and blended slag cement increases up to 28 days of immersion in 5% sodium sulphate solution and then decreases up to 90 days. Increasing of compressive strength in the presence of OPC mainly due to the continuous hydration of unhydrated cement components to form more hydration products in addition to production of Ca(OH)<sub>2</sub>, the second reaction related to the reaction between sulfate ions and hydrated cement components to form gypsum and calcium monosulfoaluminate hydrate. The decrease after 28 days mainly attributed to the second reaction and decrease in hydration of cement.

In case of blended slag cement, increasing in compressive strength occurred according to the following reactions. The first reaction attributed to continuous hydration of unhydrated cement in addition to production of Ca(OH)<sub>2</sub>, the second reaction related to the activation of slag and the formation C-S-H at early age. After 28 days, the decrease in compressive strength may be attributed to the reaction between sulfate ions with hydrated cement components to form gypsum and calcium monosulfoaluminate hydrate and this reaction continuous as shown in OPC.

**Microstructure:** As the physical properties of concrete particularly strength and permeability significantly depend on its pore structure, the application of scanning electron microscopy (SEM) will improve our ability to evaluate the effect of supplementary cementing materials on the strength and durability of the products. Figure (5 a, b, c) are shown SEM micrographs of blended slag cement and plain cement pastes immersed in 5 % sodium sulphate at 90 days for a) OPC, b) Slag A and c) Slag B.

The microstructure of the blended slag cement and plain cement pastes show the pores structure in this case which includes free lime and CSH this photo represent the area of reaction, which decreases the effect of expansion for ettringite or formation of other phases. The liberated calcium hydroxide dissolved in the pores, which increases the activation of

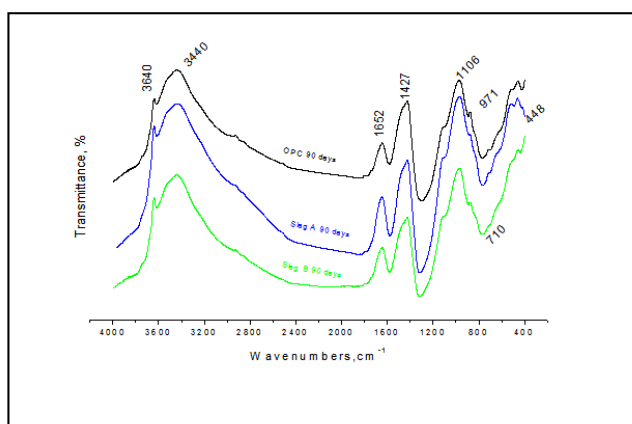
slag. Then, it is dissolved the main elements of slag in this pores. The dissolved materials react with  $\text{Ca}(\text{OH})_2$  to form calcium aluminate hydrate and calcium silicate hydrate. As reaction proceed means more accumulation of this binder phases.



**Figure 5: SEM Micrographs of Cement Pastes Immersed in 5 % Sodium Sulphate Solution at 90 days (a) OPC, (b) Slag A and (c) Slag B**

### I.R. Spectroscopy

The IR spectral for blended slag cement and plain cement pastes immersed in 5% sodium sulphate at 90 days are given in Figure 6.



**Figure 6: IR Spectral of Blended Slag Cement and Plain Cement Pastes Immersed in 5% Sodium Sulphate at 90 Days**

It is clear that, the absorption band at  $3640\text{ cm}^{-1}$  which is due to the stretch vibration of  $\text{OH}^-$  group of Portlandite (CH). The peak at  $3440\text{ cm}^{-1}$  is due to water this band increases with curing time due to the large incorporation of  $\text{H}_2\text{O}$  molecules in the formation of hydrated product. The band at  $1427\text{ cm}^{-1}$  is attributed to presence of  $\text{CaCO}_3$  (calcite), possibly formed due to carbonation of the pastes.

Furthermore, this shifted to low frequency with time due to the formation of ettringite and dissolution of free lime during the hydration process. The very sharp peak about  $1106\text{ cm}^{-1}$  pointing to the hydration of slag cement that increases with time due to the formation of (C-S-H). The hydration processes explain the formation of sharp band at  $971\text{ cm}^{-1}$  this band represents the formation of monosulphate phases which formed during the curing of samples in sodium sulphate solution. However, this peaks changed due to the formation of ettringite at later age of hydration. According to the hydration of water slag cement, the band at  $878\text{ cm}^{-1}$  represented the free Si-O which pointing to the low hydraulics



properties of water slag cement. In region of fingerprint, sulphate ions peaks formed about  $710\text{ cm}^{-1}$  is due to the diffusion of sulphate. The absorption band 458 shown the MgO band which produce in curing of sample in sodium sulphate solution.

## CONCLUSIONS

- Slag cement used as partial replacement of cement to improve properties of cement and the use of these wastes in any industry saves money and preserves the environment.
- The total Porosity of different cement paste decreases with curing time
- The compressive strength of OPC and blended slag cement increases up to 28 days of immersion in 5% sodium sulphate solution and then decreases up to 90 days.
- Increasing of compressive strength in the presence of OPC mainly due to the continuous hydration of unhydrated cement components to form more hydration products in addition to production of  $\text{Ca}(\text{OH})_2$ , the second reaction related to the reaction between sulfate ions and hydrated cement components to form gypsum and calcium monosulfoaluminate hydrate. The decrease after 28 days mainly attributed to the second reaction and decrease in hydration of cement.
- In case of blended slag cement, increasing in compressive strength occurred according to continuous hydration of unhydrated cement in addition to production of  $\text{Ca}(\text{OH})_2$ .

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